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(54) **Process for the removal of NO_x and SO_x from gas streams using a water-soluble polymeric chelate of a polyvalent metal and membrane separation means.**

(57) The invention is a cyclic proces for removing NO_x and SO_x from a gas stream. The gas stream is scrubbed with an aqueous reaction solution containing an organic, water-soluble, polymeric chelate containing a polyvalent metal ion. The NO_x is absorbed and in the presence of SO_x, the imidodisulfonate is formed. The aqueous reaction solution containing chelate and imidodisulfonate is contacted with a first separation membrane, wherein calcium oxide is added to the first permeate stream, resulting in the precipitation of calcium sulfite. The calcium sulfite is filtered from the first permeate stream, the first permeate stream combined with the first non-permeate stream, and the combined stream contacted with a second separation membrane which removes a portion of the water and other low molecular weight materials. The remaining non-permeate stream containing chelate is recycled to the scrubber. Water-soluble alkali is added to the process as needed.

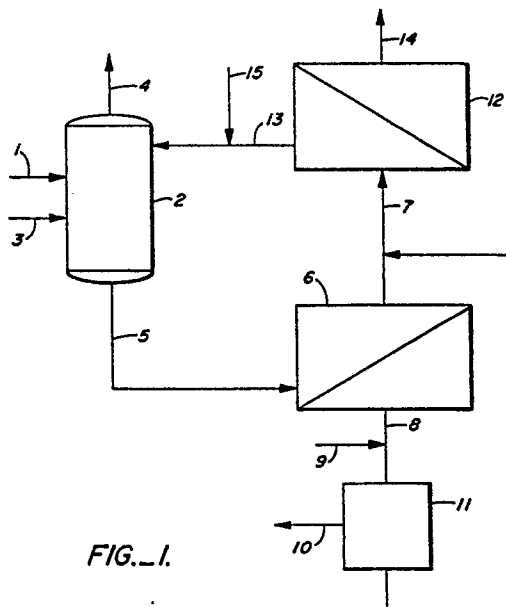


FIG. 1.

PROCESS FOR THE REMOVAL OF NO_x AND SO_x FROM GAS STREAMS USING A WATER-SOLUBLE, POLYMERIC CHELATE OF A POLYVALENT METAL AND MEMBRANE SEPARATION MEANS

This invention relates to a process for the removal of NO_x and SO_x from a gas stream using a water-soluble, polymeric chelate of a polyvalent metal and membrane separation means to recover and recycle the chelate for reuse.

The combustion of fossil fuels to generate electrical power commonly produces flue gases containing levels of NO_x (nitrogen oxides) and SO_x (sulfur oxides) which are environmentally harmful. NO_x includes NO and NO₂; SO_x includes SO₂ and SO₃. Typical flue gases may contain between about 10 and about 2000 ppmv NO_x and between about 100 ppmv and 5.0 mole percent SO_x, with SO₂ constituting the primary contaminant. The emission levels of NO_x and SO_x are subject to air quality control requirements. Methods of reducing NO_x and SO_x levels in flue gases include cleaning fuel to remove sulfur or switching to fuel containing less sulfur, controlling combustion conditions such as fuel/air ratio and temperature to minimize NO_x formation, and flue gas clean-up through scrubbing.

Common methods of removing SO_x from flue gases involve scrubbing with alkalis of calcium, magnesium, or sodium. Such methods generally are ineffective for removing NO_x from flue gases. NO_x in the presence of SO_x may be removed from flue gases by absorbing the NO_x in sulfite solutions containing iron salts to produce imidodisulfonates with subsequent hydrolysis to ammonium sulfate. NO_x may also be removed by treating flue gases with a solution containing a water-soluble monomeric or polymeric iron chelate. Problems associated with these processes include inefficient separation of excess water, excess build-up of monomeric reaction products, loss of expensive chelates, and use of expensive water-soluble alkali.

What is needed is an inexpensive process for removing NO_x and SO_x from flue gases which removes excess water and monomeric reaction products, preserves chelates within the process, and utilizes inexpensive lime as the primary source of alkali within the process.

The invention is a process for the removal of NO_x and SO_x from a gas stream containing NO_x and SO_x, comprising:

(A) contacting the gas stream containing NO_x and SO_x with an aqueous reaction solution, comprising an organic, water-soluble, polymeric chelate, wherein the chelate contains a polyvalent metal capable of absorbing NO_x, wherein the chelate possesses a molecular weight of 500 to 1,000,000, and wherein the chelate comprises a repeating polymeric chain backbone with pendant organic chemical groups capable of chelating the metal,

such that NO_x and SO_x are substantially removed from the gas stream as imidodisulfonate, sulfite, and other monomeric reaction products in the aqueous solution;

(B) separating the gas stream from which NO_x and SO_x have been substantially removed and the aqueous solution containing the chelate, imidodisulfate, sulfite, and other monomeric reaction products;

(C) contacting the aqueous solution of step (B) with a first membrane separation means to obtain:

(1) a first non-permeate stream, and

(2) a first permeate stream,

(a) adding calcium oxide to the first permeate stream precipitating substantially all of the sulfite as calcium sulfite,

(b) filtering the precipitated calcium sulfite from the first permeate stream, and

(c) combining the first permeate stream from which calcium sulfite has been precipitated and filtered with the first non-permeate stream;

wherein the combined stream contains sufficient remaining sulfite for reaction in step (A);

(D) contacting the combined first permeate and first non-permeate stream with a second membrane separation means, removing as a second permeate stream a portion of the water and other monomeric reaction products that have a molecular weight of less than 500;

(E) recycling the second non-permeate stream comprising concentrated chelate containing aqueous solution to the contacting step (A); and

(F) adding water-soluble alkali to the cyclic process.

The process of the invention removes substantially all NO_x and SO_x from flue gases while removing excess water from the process, removing excess monomeric reaction products from the process, preserving chelate within the process, and utilizing lime as the primary source of alkali within the process.

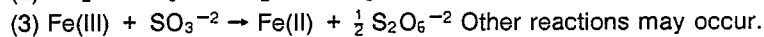
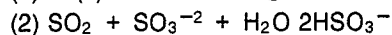
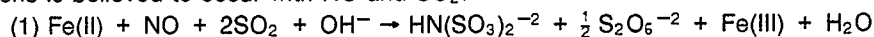
Figure 1 is a schematic representation of the inventive process.

The invention is a cyclic process to remove NO_x and SO_x from gas streams utilizing a water-soluble, polymeric chelate of a polyvalent metal, membrane separation means, and lime as the primary source of

alkali.

The gas stream containing NO_x and SO_x is contacted in a contacting zone with an aqueous reaction solution comprising an effective amount of an organic, water-soluble polymeric chelate, wherein the chelate contains a polyvalent metal capable of absorbing NO_x , wherein the chelate possesses a molecular weight
5 between about 500 and about 1,000,000, and wherein the chelate comprises a repeating polymeric chain backbone with pendant organic chemical groups capable of chelating the metal.

The contacting zone comprises any suitable gas-liquid contacting equipment, for example, a packed column, a multi-plate column, a spray tower, or a venturi scrubber. The reactions of NO_x and SO_x in the gas stream with the aqueous reaction solution results in the formation of a number of monomeric reaction
10 products, including imidodisulfonate. For example, when an iron chelate is used, the following set of reactions is believed to occur with NO and SO_2 :

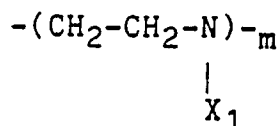


The temperature within the contacting zone is such that the reactions of NO_x and SO_x in the gas stream react with the aqueous reaction solution in a reasonable time. The temperature is preferably in the range of 10 to 90°C, more preferably in the range of 10 to 60°C. The residence time within the contacting zone is such that the reactions of NO_x and SO_x in the gas stream with the aqueous reaction solution are substantially complete. Preferably the residence time in the contacting zone is less than about 15 minutes,
20 more preferably less than about 5 minutes. The ratio of gas flowrate/aqueous reaction solution depends upon the concentration of NO_x and SO_x in the gas stream and the concentration of chelate in the aqueous reaction solution. Preferably the ratio of gas flowrate/aqueous reaction solution is in the range of 10 to 1,000 SCFM/GPM. The concentration of chelate in the aqueous reaction solution is that which is sufficient to react with the NO_x present in the gas stream. The concentration of chelate depends also on the particular chelate
25 used. In the case of iron chelates, for example, the concentration of chelating groups is preferably in the range of 0.01 to 0.5 Molar.

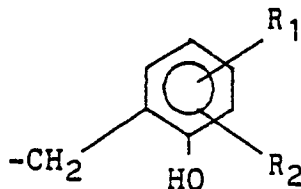
Any inert, water-soluble, polymeric chelate capable of chelating a polyvalent metal is suitable in the present process. Inert in this context is defined as not detrimentally reactive in the reaction to an intolerable extent. Polymeric chelates possessing a molecular weight of 500 to 1,000,000 are preferred in the present
30 process. Polymeric chelates possessing a molecular weight between 1000 and 500,000 are more preferred.

Water-soluble polymeric chelates possessing a backbone chain with pendant groups capable of chelating polyvalent metals are preferred. More preferred water-soluble polymeric chelates possessing pendant polyvalent metal chelating groups include, for example, the following repeating polymeric groups:

(a)



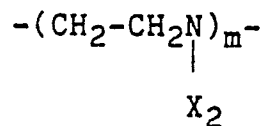
wherein X_1 is independently in each occurrence -H, $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$, or



wherein

R_1 and R_2 are independently in each occurrence $-\text{CH}_3$, $-\text{SO}_3\text{H}$, $-\text{Cl}$, $-\text{H}$, $-\text{COOH}$ and m is an integer between 5 and 20,000;

(b)

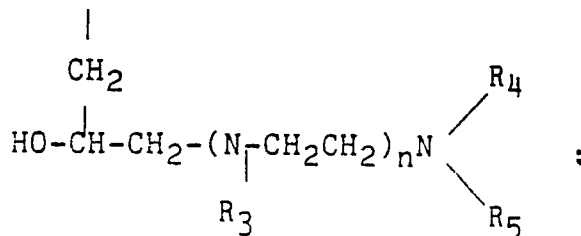


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wherein

X₂ is independently in each occurrence -H, -CH₂CH(OH)CH₂OH, -CH₂CH(OH)CH₂Cl, or

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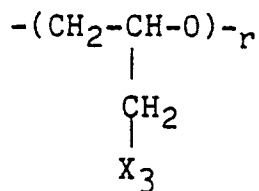
R₃, R₄ and R₅ are independently in each occurrence X₁, wherein X₁ is as defined hereinabove;

20 m is an integer between 5 and 20,000; and

n is 0, 1, 2, 3 or 4;

(c)

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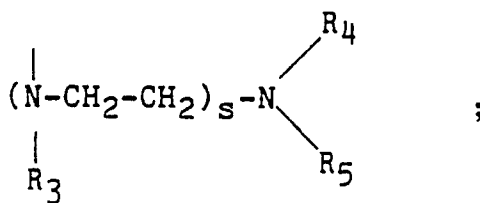


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wherein

X₃ is independently in each occurrence -OH, -Cl, or

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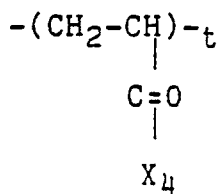
R₃, R₄ and R₅ are as defined hereinabove;

45 r is an integer between 10 and 20,000, and

s is an integer between 1 and 4;

(d)

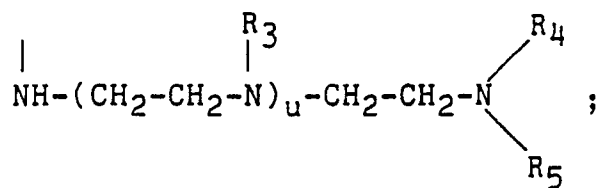
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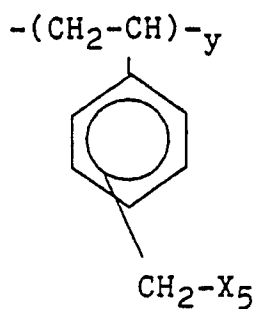
wherein

X₄ is independently in each occurrence -OH, -OCH₃, -OCH₂CH₃, or



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10 R_3 , R_4 and R_5 are as defined hereinabove;
 t is an integer between 10 and 20,000, and
 u is an integer between 1 and 4;
 (e)

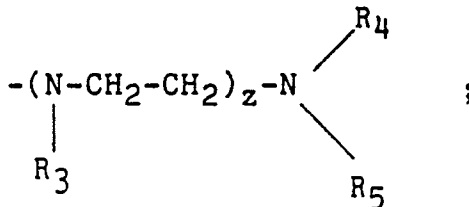


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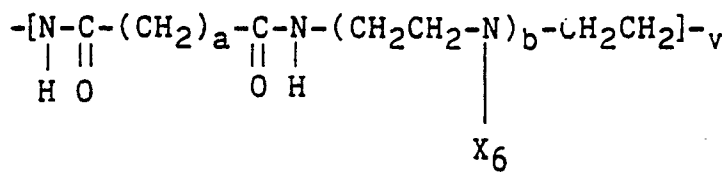
wherein
 X_5 is independently in each occurrence -OH, -Cl, or



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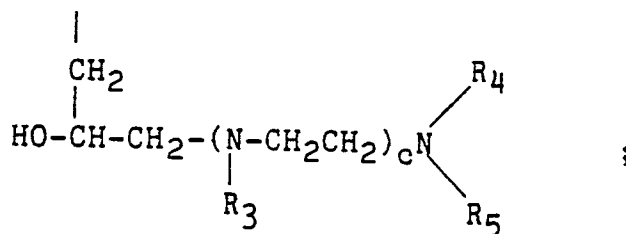
R_3 , R_4 and R_5 are as is defined hereinabove;
 y is an integer between 10 and 20,000, and
 z is an integer between 1 and 4;
 (f)



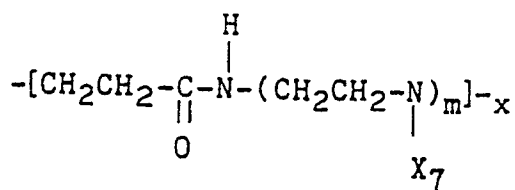
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wherein
 50 X_6 is independently in each occurrence -H, - $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, - $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$, or

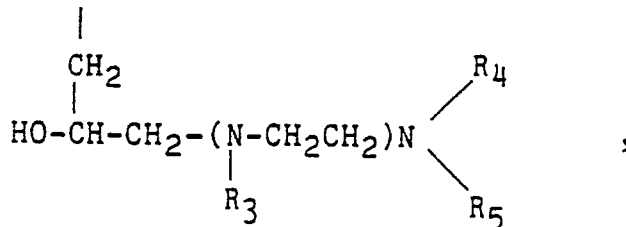
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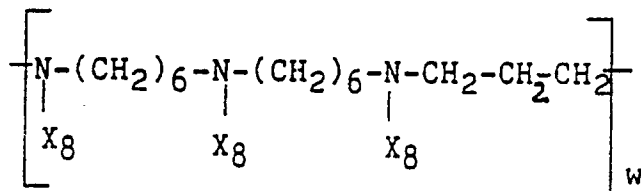
- 10 R_3 , R_4 and R_5 are as defined hereinabove;
 v is between 10 to 10,000,
 a is 6,
 b is between 1 and 4, and
 c is between 1 and 4;
 15 (g)



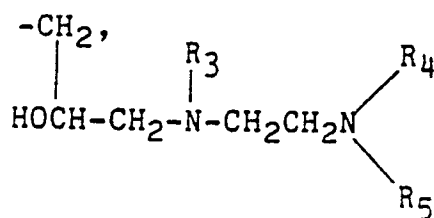
- 25 wherein
 X_7 is independently in each occurrence -H, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$, or



- 35 m , x , and n and R_3 , R_4 and R_5 are as defined hereinabove; or
 (h)



- 45 wherein X_8 is independently in each occurrence -H, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{CH}(\text{OH})$, or



wherein

R₃, R₄ and R₅ are as defined hereinabove; and
w is between 2000 and 4000.

Mixtures of the organic water-soluble polymeric chelates described hereinabove are also useful in the present invention.

A more detailed description of the preparation of the hereinbefore described water-soluble organic polymeric chelates is provided below and as part of the Examples. Some polyamines and polyethers used in synthesis are described in Table 1.

TABLE 1

POLYAMINES USED AS STARTING MATERIALS FOR POLYCHELATOR SYNTHESIS			
Amine ^a	Degree of Polymerization (D.P.)	Molecular Weight Range	Nature of Chain
E-100 ^b	67.5	250-3000.28	Branched
PEI-6	154	6007.3	Branched
Hydrolyzed PEOx	50 ^c	2000	Linear
Purifloc C-31 ^d	500	10,000-30,000	Branched
Hydrolyzed PEOx	500 ^f	20,000	Linear
PEI-600	1500	60,000	Branched
Hydrolyzed PEOx	5000 ^g	500,000	Linear

a. PEI = polyethyleneimine; PEOx, polyethyloxazoline. PEI is a polymer of molecular weight 60,000 (CORCAT 600) and is obtained from Cordova Chemical Company. The nitrogen content is determined by drying a sample and elemental analysis of the solid.

b. E-100 -- is a byproduct of ethylenediamine manufacture and is a low molecular weight branched polymer containing about six ethyleneamine groups.

c. 100 percent hydrolyzed.

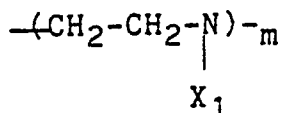
d. Purifloc C-31 -- is a polyethylene amine product of The Dow Chemical Company, Midland, Michigan.

e. Probably also partially crosslinked.

f. 85 percent hydrolyzed.

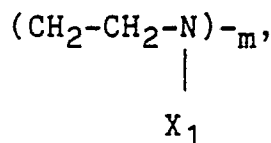
g. 97 percent hydrolyzed.

One embodiment of the chelate designated (a)



wherein X₁ is -H or -CH₂COOH (CHELATE A) is prepared by dissolving polyethyleneimine (CORCAT 150 or CORCAT 600, available from the Cordova Chemical Company) in water, followed by reaction with excess sodium chloroacetate in the presence of strong base.

Another embodiment of the polymeric chelate designated (a)

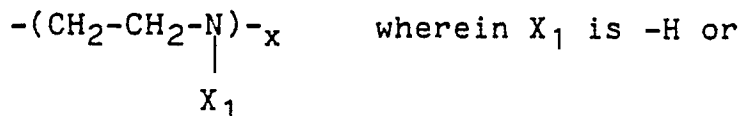


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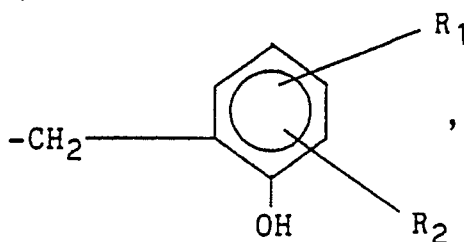
wherein X_1 is -H or $-\text{CH}_2\text{P}(=\text{O})(\text{OH})_2$ (CHELATE B) is prepared by dissolving polyethyleneimine in water and reacting with phosphoric acid and formaldehyde. The process described by R. S. Mitchell in U.S. Patent 3,974,090 for the monomer may be adapted using the polymeric imine.

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A further embodiment of the polymeric chelate designated (a)



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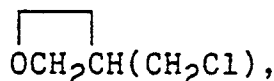
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and R_1 , R_2 are each methyl (CHELATE C) is obtained by dissolving polyethyleneimine in water followed by treatment with 2,4-dimethylphenol and formaldehyde. The general procedure described by G. Grillot and W. Gormley, Jr., J. Amer. Chem. Soc., Vol. 67, pp. 1968ff (1945) for the monomer is adapted using the polymeric imine.

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One embodiment of the polymeric chelate designated (b) wherein X_2 is -H or $-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2\text{NR}_3\text{CH}_2\text{CH}_2-\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ and n is 1 (CHELATE D) is obtained by first reacting triacetic acid to produce epichlorohydrin,



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with ethylenediamine-



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followed by reaction with polyethyleneimine. The procedure described above, for CHELATE A, may also be adapted. For those polymers wherein n is 2, 3 or 4, the ethylenediamine is replaced with the corresponding diethylenetriamine, triethylenetetraamine, or tetraethylene-pentamine, respectively.

Another embodiment is of the polymeric chelate designated (b) wherein m is about 20,000, n is 0, X_2 is -H or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NR}_3\text{CH}_2\text{CH}_2-\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ (CHELATE D-1), iminodiacetic acid is dissolved in water and epichlorohydrin, about a 20 percent excess is added. The product is extracted with a chlorinated hydrocarbon such as methylene chloride to remove the unreacted epichlorohydrin. To this aqueous solution is added a 33 percent aqueous solution of polyethyleneimine, e.g., CORCAT 600. The solution is heated and further treated with sodium hydroxide at a pH of 9-10. The chelate solution is used without further purification.

45

One embodiment of the polymeric chelate designated (c) wherein X_3 is -OH or $-(\text{NR}_3\text{CH}_2)\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ (CHELATE E) is prepared by treating polyepichlorohydrin with ethylenediamine in the presence of base followed by treatment with excess sodium chloroacetate.

One embodiment of the chelate designated (d) wherein t is 100, u is 1, X_4 is -OH or $-\text{NHCH}_2\text{CH}_2\text{NR}_3\text{CH}_2\text{CH}_2\text{NR}_4\text{R}_5$, and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ (CHELATE F) is prepared by the treatment of poly(ethylacrylate) with diethylenetriamine followed by treatment with sodium chloroacetate in the presence of a strong base.

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One embodiment of the chelate designated (e) wherein X_5 is -OH or $-\text{NR}_3\text{CH}_2\text{CH}_2\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$, y is 100 and z is 1 (CHELATE G) is the treatment of poly(vinylbenzylchloride) with

ethylenediamine in the presence of strong base. The product in the presence of base is then treated with excess sodium chloroacetate. By replacement of ethylenediamine with diethylenetriamine, triethylene tetraamine, and the like, the higher homologs are produced.

One embodiment of the chelate designated (f) wherein X_6 is -H or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NR}_3-\text{CH}_2\text{CH}_2\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ and c is 1 (CHELATE H) is obtained by the treatment of the commercial polymer KYMENE 557H which is obtained from the Hercules Corporation of Wilmington, Delaware, with ethylenediamine triacetic acid.

One embodiment of the chelate designated (g) wherein X_7 is -H or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NR}_3\text{CH}_2\text{CH}_2\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each $-\text{CH}_2\text{COOH}$ and n is 1 (CHELATE J), is obtained by reacting the polymer of methylacrylate and ethylenediamine with the epoxide adduct formed by the treatment of iminodiacetic acid with epichlorohydrin.

One embodiment of the chelate designated (h) wherein X_8 is -H, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$, or $-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2\text{NR}_3\text{CH}_2\text{CH}_2\text{NR}_4\text{R}_5$ and $\text{R}_3, \text{R}_4, \text{R}_5$ are each CH_2COOH , is obtained by reacting the commercially available FIBRABON 35 from the Diamond Shamrock Co., Cleveland, Ohio with ethylenediamine-triacetic acid in the presence of base (CHELATE K).

A more detailed description of the preparation for these organic water-soluble polymeric chelates is provided as part of the Examples.

Generally, any polyvalent metal can be used in the present invention as the metal component of the polymeric chelate to remove NO. Iron, copper, cobalt, and manganese are preferred. Iron is especially preferred. The polyvalent metal chelate should be preferred. The polyvalent metal chelate should be capable of acting as a catalyst to instantaneously complex NO and should then be capable of regeneration.

The gas stream from which NO_x and SO_x have been substantially removed is separated from the aqueous solution containing the chelate, imidodisulfonate, and other monomeric reaction products. The aqueous solution is contacted with a first membrane separation means to obtain a first non-permeate stream and a first permeate stream. An effective amount of calcium oxide (lime) is added to the first permeate stream to precipitate substantially all of the sulfite present in the first permeate stream as calcium sulfite. The amount of calcium oxide added depends upon the concentration of sulfite in the first permeate stream; 1 mole of calcium oxide is required to precipitate 1 mole of sulfite as calcium sulfite. The calcium sulfite precipitate is removed from the first permeate stream by filtration. The first permeate stream is then combined with the first non-permeate stream. The sulfite remaining in the combined first permeate and first non-permeate stream should be sufficient for reaction in the NO_x and SO_x containing gas stream/aqueous reaction solution contacting zone. Preferably this results in 15 to 70 volume percent, more preferably 30 to 70 volume percent, of the aqueous solution passing through the recycle loop as the first permeate stream.

The first membrane separation means is preferably ultrafiltration or dialysis, more preferably ultrafiltration. The membranes useful in this invention may be in flat sheet, tubular, or hollow fiber form. The membranes are formed from polymers which are not deleteriously affected under conditions of use, for example, polysulfones, polyethersulfones, polyamides, cellulosic polymers, polyetherketones, polyolefins, polycarbonates, polyesters, polyestercarbonates, and the like. The membranes preferably possess a molecular weight cutoff such that substantially all of the chelate is retained in the first non-permeate stream. The molecular weight cutoff of the membrane will therefore depend upon the molecular weight of the chelate used. The molecular weight cutoff of the membranes useful in this invention preferably is in the range of 500 to 30,000. The water flux through the membrane should occur at reasonable rates while retaining substantially all of the chelate in the non-permeate stream. The water flux through the membranes is preferably in the range of 5 to 100 GFD. The membrane separation occurs at temperatures and pressures which do not deleteriously affect the membrane. The membrane separation temperature is preferably 0 to 90°C, more preferably 10 to 60°C, even more preferably 10 to 45°C. The membrane separation pressure is preferably 5 to 100 psi.

The combined first permeate and first non-permeate stream is contacted with a second membrane separation means to remove a portion of the water and monomeric reaction products in a second permeate stream and to recover substantially all of the chelate in the second non-permeate stream which is recycled to the NO_x and SO_x containing gas stream/aqueous reaction solution contacting zone for reuse. Preferably this results in 5 to 25 volume percent of the combined first permeate and first non-permeate stream being withdrawn as a second permeate stream. The second membrane separation means and the conditions of membrane separation are as described for the first membrane separation means.

An effective amount of water-soluble alkali is added to the cyclic process. The water-soluble alkali is preferably added to the cyclic process at a point just prior to or within the NO_x and SO_x containing gas stream/aqueous reaction solution contacting zone. The water-soluble alkali may be for example Na_2CO_3 - (soda ash) or NaOH. The water-soluble alkali is added in an amount sufficient for the reactions in the

contacting zone.

In Figure 1, the NO_x and SO_x containing gas stream (1) is introduced into the gas stream/aqueous reaction solution contacting zone (2). Fresh or make-up aqueous reaction solution (3) may be introduced into the contacting zone (2). The purified gas stream (4), substantially free of NO_x and SO_x, is separated from the aqueous solution and is removed from the gas stream/aqueous reaction solution contacting zone (2). The aqueous solution containing chelate, iminodisulfonate, and other monomeric reaction products (5) is passed to a first membrane separation means (6) in which the aqueous stream (5) is split into a first non-permeate stream (7) and a first permeate stream (8). Calcium oxide (9) is added to the first permeate stream (8), resulting in the precipitation of calcium sulfite (10) which is removed from the first permeate stream (8) by filtration (11). The first permeate stream from which substantially all of the sulfite has been removed is then recombined with the first non-permeate stream (7). The combined first permeate and first non-permeate stream is passed to second membrane separation means (12) which separates the combined first permeate and first non-permeate stream into a second non-permeate stream (13) and a second permeate stream (14). Substantially all of the chelate remains in the second non-permeate stream (13) which is recycled back to the gas stream/aqueous reaction solution contacting zone (2). The second non-permeate stream (14) removes excess water and monomeric reaction products from the process. Water-soluble alkali (15) may be added to the process just prior to or within the gas stream/aqueous reaction solution contacting zone (2).

The following Examples are to be construed as being illustrative and are not to be limiting in any way.

Example 1 - Preparation of Polymeric Chelate (a) Based on Polyethyleneimine (PEI)

[CHELATE A]

(a) Polyethyleneimine, about 11 grams, degree of polymerization (DP) 1500, is dissolved in water (about 200 ml) to produce a solution of about 1.25 molar (in amine nitrogen). To the aqueous solution is added sodium chloroacetate (about 31 grams, a 5 percent excess) with stirring while maintaining the reaction mixture at about 60° C. A pH electrode is used to monitor the reaction and about 50 weight percent sodium hydroxide is added to maintain the pH above about 10. After 40 minutes of reaction the reaction is complete, and the reaction mixture is allowed to cool. The aqueous solution is diluted to about 1.0 M (amine nitrogen) and used without further purification.

Example 1A - Preparation of Polymeric Chelate (a)

[CHELATE B]

To a 500 ml flask equipped with a water condenser and dropping funnel is added 99 grams (0.6 mole) of 49.9 weight percent ortho-phosphorous acid (which also contains 9.4 grams of hydrogen chloride) and 5.2 grams of 37 weight percent hydrochloric acid. The total moles of hydrogen chloride used is 0.4. The resultant mixture is then allowed to heat by the addition of 14 grams of CORCAT 150 (Cordova Chemical Co.) as an 33 weight percent aqueous solution of polyethyleneimine containing 0.1 mole of amine nitrogen. The polyamine is added over a period of 8 to 10 minutes while the reaction mixture achieves a temperature of 70-75° C. The reaction mixture is then heated for 20 minutes to the boiling temperature, thereby producing a homogeneous clear solution having a boiling point of between 110-115° C. The resulting clear aqueous solution is maintained at boiling for 2 hours, and 22 grams (0.66 mole) of paraformaldehyde is added. After 2 hours, the clear reaction mixture is kept boiling for an additional 30 minutes and cooled to 25-30° C. The clear solution has an amber color, and contains 50 weight percent of the polyethyleneimine phosphonate which is used without further purification.

Example 1B - Preparation of Polymeric Chelate (a)

[CHELATE C]

To a 13 gram aqueous solution (33 weight percent) of polyethyleneimine CORCAT 150 (from Cordova Chemical Company) containing 0.1 mole of available amine nitrogen is added 10.8 grams of p-cresol (0.1 mole). The solution is maintained below 20 °C, while a 37 weight percent aqueous formaldehyde solution (0.11 mole) is added slowly with stirring. The solution is allowed to stand for an hour at ambient temperature and then warmed to 80 °C for 2 hours. The aqueous solution is used without purification in subsequent experiments.

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Example 2 - Preparation of Polymeric Chelate (b)

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[CHELATE D]

This preparation is performed in two steps: (1) attachment of ethylenediamine to the polymer; and (2) conversion of the amine to the ED3A.

Step 1: 23.5 grams of polyepichlorohydrin (0.25 Mole monomer unit) and 94 grams of 85 weight percent ethylenediamine (1.3 moles) are dissolved in 50 ml isopropanol and 25 ml of toluene and refluxed at 100 °C for six hours. As the reaction proceeds, additional isopropanol is added to maintain homogeneity, with the final system being 75/25 weight percent isopropanol/toluene. The reaction is followed by titrating aliquots for chloride ion with silver nitrate. Next, 20 grams of 50 weight percent NaOH (0.25 mole) is added, the solid NaCl formed is filtered, washed with ethanol, and the liquid is removed in a vacuum evaporator at 55 °C. Although some NaCl remains in the product, the elemental analysis gives a C:H:N mole ratio of 4.6:12.1:2.00 (expected mole ratio is 5:12:2).

Step 2: This intermediate is taken up in 200 ml of water, to which 3.3 moles of sodium chloroacetate is added per mole of nitrogen. The system is kept at 60 °C and a pH of 10 for one hour. At this point, a white precipitate (presumably NaCl) is filtered off, the pH is adjusted to 2 (the expected isoelectric point), at which point considerable white solid forms. This solid is filtered and found to be EDTA, presumably formed because all of the unreacted ethylenediamine had not been removed during the vacuum evaporation. The filtrate is dialyzed against 4 liters of water.

An estimate of the ethylenediaminetriacetic acid content of the dialyzed (polymeric) material is made by titrating an aliquot with iron (III). One-third of the expected chelant groups are found in the polymer fraction.

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Example 2A - Preparation of Polymeric Chelate (b)[CHELATE D-1]

14.3 grams (0.1 mole) of iminodiacetic acid is dissolved in 100 ml of water. To this solution is added 0.12 mole epichlorohydrin, a 20 percent excess. After allowing the solution to stand for an hour at ambient temperature, it is extracted with 50 ml of methylene chloride to remove the unreacted epichlorohydrin. To the aqueous phase from this extraction is added 14.7 grams of a 33 weight percent solution of polyethyleneimine CORCAT 600 (Cordova Chem. Co., Muskegon, Michigan), an amount determined to contain 0.1 mole of nitrogen. The solution is heated to 60 °C, while sodium hydroxide solution (10 N) is added at a rate sufficient to maintain the pH in the range of 9-10. After 30 minutes, the reaction is complete and the resulting solution, which now contains the polyethyleneimine with iminodiacetic acid groups attached to it, is used without purification in subsequent experiments.

Example 3 - Preparation of Polymeric Chelate (c)[CHELATE E]

22.4 grams (0.1 mole) of ethylenediamine triacetic acid is dissolved in 100 ml of water. To this solution is added 0.12 mole of polyepichlorohydrin (HYDRIN 10 x 1 DP ~ 40), (B.F. Goodrich, Cleveland, Ohio), a 20 percent excess in 100 ml of toluene/methylene chloride (50/50; v/v). To this two-phase solution is added 0.01 mole of tetrabutyl ammonium chloride as a phase transfer catalyst. The solution is allowed to stir vigorously for an hour at ambient temperature. The HCl produced is taken up by the addition of sodium hydroxide. The aqueous polymeric chelate is subsequently used without purification.

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Example 4 - Preparation of Polymeric Chelate (d)

[CHELATE F]

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Poly(methylacrylate), 86 grams, equivalent to one mole of formula weight of the monomeric methyl acrylate, is dissolved in 300 ml of toluene, and 520 grams of diethylenetriamine (5 moles) are added. The solution is heated to 40-50 °C for an hour and the excess amine and toluene are evaporated under vacuum. The residue is taken up in 500 ml of water and 348 grams of sodium chloroacetate (3.0 mol) are added to the solution, and heated to 60 °C for 30 minutes while sodium hydroxide is added at a rate sufficient to maintain the pH at 9-10. This solution, which has the desired structure, is used without further purification in subsequent experiments.

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Example 5 - Preparation of Polymeric Chelate (e)

[CHELATE G]

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Polyvinylbenzyl chloride, 15 grams, equivalent to 0.1 mole of monomer units, is dissolved in 100 ml of methylene chloride, and 30 grams of ethylene diamine (0.5 mole) are added. The solution is warmed to 40 °C and stirred for 2 hours. The excess amine and methylene chloride are evaporated under vacuum. The resulting polymer is taken up in 200 ml of water and carboxymethylated as in the preceding example. The resulting polymer has the desired structure and is used further without purification.

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Example 6 - Preparation of Polymeric Chelate (f)

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[CHELATE H]

80 grams of the polymer KYMENE 557H (0.1 mole monomer equivalent) (Hercules Corporation, Wilmington, Delaware), which is a copolymer of adipic acid, diethylenetriamine and epichlorohydrin, is added to a solution of 46 grams of ethylenediaminetriacetic acid in 200 ml of water (a twofold excess). The solution is heated to 80 °C for two hours. The resulting solution, which contains the desired polymer (vi), is used without further purification in subsequent experiments.

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Example 7 - Preparation of Polymeric Chelate (g)

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[CHELATE J]

A solution of an adduct of epichlorohydrin and iminodiacetic acid, as prepared in Example 2A, is added

to an equimolar quantity of a polymer solution made by reacting equimolar quantities of methyl acrylate and ethylenediamine. The solution is heated to 80°C for 2 hours and the resulting polymer is used in subsequent experiments.

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Example 8 - Preparation of Polymeric Chelate (h)

[CHELATE K]

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54 grams of the commercial polymer FIBRABON 35 (Diamond Shamrock Corporation, Cleveland, Ohio), which contains 100 millimoles of active epichlorohydrin groups, is mixed with a solution of 46 grams of ethylenediaminetriacetic acid (0.2 mole). The solution is heated to 60°C and sodium hydroxide is added at a rate sufficient to maintain the pH at 9-10. After 2 hours, the reaction is complete, and the solution is used in subsequent experiments.

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Example 9 - Chelation of Iron (II) by Polymeric Chelating Agents

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Various polymeric chelates are obtained by treating the polymeric chelant with iron at pH 7. The results of these reactions is shown in Table II.

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TABLE II

CHELATION OF IRON (II) BY POLYMERIC CHELATING AGENTS		
Ratio W is the mole ratio of nitrogen in chelating monomer or polymer to iron at point of incipient precipitation at room temperature. pH in all tests is 7 ± 0.5 .		
Chelator	(Fe), Molar	W
EDTA	0.03	2.0
MBEDTA	0.03	2.2
Sym. EDDA	0.03	10
DTDA	0.015	9
DTPA	0.03	2.5
TTHA	0.05	2.3
CM E-100	0.04	3.4
CM PEI 6	0.045	3.2
CM PEOx, DP-50	0.025	5
CM PEOx, DP-1000	0.025	4
CM PEOx, DP-10,000	0.015	4.2
CM C-31 (Dow Chemical)	0.04	5
EDTA - Ethylenediamine tetracetic acid MBEDTA - Methyl-p-benylethylenediaminetriacetic acid Sym. EDDA - Sym. Ethylenediaminediacetic acid DTPA - Diethylenetetraaminepentaacetic acid DTDA - Diethylenetriamenediacetic acid TTHA - Triethylenetetraaminehexaacetic acid CM - Carboxymethyl PEI - Polyethyleneimine PEOx - Polyethyleneoxazoline		

Example 10 - NO Absorption Using Polymeric Chelate of Iron (II)

A number of polymeric chelates containing iron (II) are treated with NO in aqueous solution. The results are shown in Table III, wherein the mole ration of NO to iron (II) is shown. The polymeric chelates absorb NO to an extent comparable to the monomeric chelates.

TABLE III

NITRIC OXIDE ABSORPTION BY IRON (II) CHELATES				
Chelator	Mole Ratio, N/Fe	Final pH	NO Absorbed mol/mol Fe	Appearance of Final System
None	-	6.8	0.03	ppt. present
HEIDA	1	7.6	0.1	some blue floc.
Sym. EDDA	2	7.2	0.4	much blue floc.
EDTA	2	7.1	0.067	clear, brown-green
HEDTA	2	6.8	0.37	clear, brown-green
DTDA	3	7.0	0.23	clear, brown-green
DTDA	3	7.2	0.37	much blue floc.
DTDA	3	7.5	0.007	clear, yellow
TTHA	2	6.3	0.20	clear
CM E-100	2	6.8	0.07	much blue floc.
CM E-100	4	6.7	0.07	clear
CM PEI 6	2	7.4	0.17	much floc.
	3	7.2	0.10	much floc.
	4	7.0	0.10	clear, brown-green
	18	7.1	0.03	clear, yellow-green
CM PEOx, DP 50	2	7.2	0.13	much floc.
	2	7.5	0.28	much floc.
	4	7.3	0.07	small amount floc.
CM PEOx, DP 500	2	6.6	0.03	no observ.
CM C-31	2	6.7	0.08	much floc.
CM C-31	4	7.1	0.07	clear
Reaction conditions:				
120 ml of 0.025 M Fe(II) sulfate. Temperature 55° C.				
Gas flow: 1.2 liters/min. nitrogen containing 250 ppm. NO.				

Example 11 - Dialysis of Iron Polymeric Chelating Agents

In the dialysis, 100 ml of iron (II) organic chelate, made up to be 0.1 molar in iron, is dialyzed into two liters of deionized water overnight. The CM PEI 150 and CM PEI 600 polymeric chelating agents are dialyzed through a SPECTROPOR 1 membrane, available from Van Waters & Rogers, San Francisco, California, which has a nominal molecular weight cut-off of 6000-8000. In both cases, 3-5 weight percent of the iron is lost. The CM PEI 6 solution is dialyzed through a SPECTROPOR 6 membrane (Van Waters & Rogers) which has a cut-off of 2000. In this case 10 weight percent of the iron is lost.

Example 12 - Ultrafiltration of Iron Polychelates

The ultrafiltration tests are performed in an Amicon Model 52 cell which is a cylindrical chamber with a 43 mm diameter membrane as the bottom surface. The cell volume is 60 ml and the cell contains a suspended magnetic stirring bar to reduce polarization effects. In a run, a 25-ml volume of solution is placed in the cell and the gas space is connected to an air line maintained at 15 psi (103.4 kPa).

Three membranes are used for this study, all obtained from the Amicon Corporation of Danvers, Massachusetts. They are designated as UM 05, UM 2 and PM 10, having nominal molecular weight cutoffs of 500, 1000 and 10,000, respectively. The iron is determined by the standard thiocyanate method.

The results are shown in Table IV.

TABLE IV

ULTRAFILTRATION AND DIALYSIS OF IRON POLYCHELATES					
	UM 05	UM 2		PM 10	
Polychelator	Rejection %	Rejection %	Flow *GFD (L/m ² d)	Rejection %	Flow *GFD (L/m ² d)
CM PEI 600	89	98	1.3 (52.9)	91	6 (244.1)
CM PEI 600 (dialyzed)		99	2.8 (113.9)	95	16 (651.0)
CM PEI 150 (dialyzed)		95	1.4 (57.0)	97	9 (366.2)
CM PEI 6		80-90	0.8 (32.6)	25	28 (1139.3)
CM PEI 6 (dialyzed)	61	90	<0.3 (<12.2)		
CM E-100	84	92	0.6 (24.4)	27	40 (1627.6)
EDTA	23	10	1 (40.7)		
Deionized					
H ₂ O only			5 (203.4)		
[CM PEI -- Carboxymethyl polyethyleneimine, etc.]					
Rejection % values are averages over steady state portion of run.					
Flow values are interpolated or extrapolated to 0.10 M Fe.					
Rejection percent -- the amount of chelate (or material) which did not pass through the membrane.					
*GFD = gal/(ft ² x day)					

As can be seen from Table IV, polychelates based on carboxymethylated polyethyleneimine 6 (CM PEI 6, 15 onomer units) or larger polymers are fairly well rejected by ultrafiltration membranes having cut-offs in the molecular weight range of 1000-10,000. CM PEI 6 is strongly rejected (80-90 percent) by Amicon UM 2 membrane (having a cut-off value of 1000), but poorly (20-30 percent) by PM 10 (cut-off 10,000). Higher polymers CM PEI 150 and CM PEI 600 are both strongly rejected 95-99 percent by both membranes.

At a concentration of 0.1 M chelated iron (III) output from an Amicon UM 2 membrane is 1 gallon per square foot per day (GFD) (40.1 L/m²d) with the polychelators of Table III at a pressure of 15 psi (103.4 kPa). For the PM 10 membrane, the output is 6-30 GFD (244.1-1220.7 L/m²d). Output is strongly dependent upon iron concentration.

Example 13 - Adsorption of NO with Polymeric Chelate of Fe(II) and Separation

The polymeric chelate of Example 1 containing Fe(II) at a concentration of 0.025M in Fe(II) and 0.050M in S₂O₃⁼ is dialyzed using a Spectrapor 6 membrane (2000 MW cut-off), area 4.5 cm². Na₂SO₄ (0.050M) is used as the dialysate solution. 100 ml of dialysate is used. The permeability of the Fe(II)-chelate is 0.7 x 10⁻² cm/hr and for S₂O₃⁼ is 0.6 cm/hr.

Additional permeabilities are obtained using the Fe(II) and Fe(III) chelate shown in Table V.

TABLE V

PERMEABILITIES OF IRON CHELATES AND THIOSULFATE THROUGH A DIALYSIS MEMBRANE					
Spectrapor 6 membrane (2000 MW cut-off), Area = 4.5cm ²					
Fe CHELATE	FEED Conc. M	(S ₂ O ₃) ⁼ M	DIALYSATE ml	P, CM/HR. Fe	S ₂ O ₃ =
--	--	0.10	~80	--	0.5
Fe III-EDTA	0.050	0.050	~90	22 x 10 ⁻²	1.1
Fe III-CME-100	0.025	0.050 ^(a)	100	0.7 x 10 ⁻²	0.6
Fe III-CME-100	0.025	0.050 ^(a)	100	3.6 x 10 ⁻²	0.6
Fe III-CM PEI 6	0.06	--	90	0.37 x 10 ⁻²	--

(a) 0.050M Na₂SO₄ used as dialysate solution; water used in other systems.

It is apparent from Table V that the polymeric chelates are not separated by dialysis through the membrane to the extent that the monomeric chelate is dialyzed.

Example 13 - Removal of NO and SO₂

A gas stream from an oil combustion unit having a concentration of NO of 0.011 weight percent and SO₂ of 0.03 weight percent enters a contact vessel which contains an aqueous solution containing 1.0 percent by weight of iron (II) (based on the total weight of the mixture) as the polymeric chelate of carboxymethyl polyethyleneimine CM PEI 6. The chelate is supplied at 50 percent molar excess based on iron and the pH of the system is 7. The pressure of the fluid gas is 15 psi (103.4 kPa) and the temperature of the reaction is 55 °C. A contact time of 60 seconds is used. The NO and SO₂ are converted to HN(SO₃)₂⁼, which remains in solution. The aqueous solution is then subjected to ultrafiltration using an Amicon UM 2 membrane and apparatus. The CM PEI 6 is retained in the aqueous solution while the low molecular weight water and HN(SO₃)₂⁼ are separated. The retained aqueous solution containing the CM PEI 6 Fe(II) is recycled to the contact vessel.

Example 14 - Removal of NO and SO₂

The process scheme of Figure 1 is used to treat a flue gas stream of 2x10⁶ SCFM (5.7 x 10⁴ m²/min.) containing 326 ppm NO and 1832 ppm SO₂. The flue gas is contacted with 20,000 GPM (75,700 L/min.) of an aqueous stream containing 5 weight percent concentration of CHELATE K of Example 8 of molecular weight 20,000. 90 percent of the NO and 99 percent of the SO₂ is removed from the flue gas. The aqueous stream containing chelate, imidodisulfonate, and other monomeric reaction products is then contacted with an Amicon polysulfone microporous ultrafiltration membrane possessing a molecular weight cut-off of 10,000. A portion of the aqueous stream is obtained as permeate, to which lime is added to precipitate calcium sulfite, which is removed from the permeate by filtration. The filtered permeate is then combined with the non-permeate prior to contacting the combined non-permeate and filtered permeate stream with an Amicon polysulfone ultrafiltration membrane possessing a molecular weight cut-off of 10,000. 5-25 weight percent of the aqueous stream containing 0 weight percent of the chelate, is withdrawn as permeate. The non-permeate is recycled back to the gas stream/aqueous stream contacting zone.

Claims

1. A process for the removal of NO_x and SO_x from a gas stream containing NO_x and SO_x , comprising:

(A) contacting said gas stream with an aqueous reaction solution comprising an organic, water-soluble, polymeric chelate, wherein the chelate contains a polyvalent metal for absorbing NO_x , wherein the chelate possesses a molecular weight of 500 to 1,000,000, and wherein the chelate comprises a repeating polymeric chain backbone with pendant organic chemical groups capable of chelating the metal, such that NO_x and SO_x are substantially removed from the gas stream as imidodisulfonate, sulfite, and other monomeric reaction products in the aqueous solution;

(B) separating the gas stream from which NO_x and SO_x have been substantially removed and the aqueous solution containing the chelate, imidodisulfate, sulfite, and other monomeric reaction products;

(C) contacting the aqueous solution of step (B) with a first separation membrane to obtain:

(1) a first non-permeate stream, and

(2) a first permeate stream,

(a) adding calcium oxide to the first permeate stream, precipitating substantially all of the sulfite as calcium sulfite,

(b) filtering the precipitated calcium sulfite from the first permeate stream, and

(c) combining the first permeate stream from which calcium sulfite has been precipitated and filtered with the first non-permeate stream,

wherein the combined stream contains sufficient remaining sulfite for reaction in step (A);

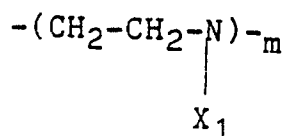
(D) contacting the combined first permeate and first non-permeate stream with a second separation membrane, removing as a second permeate stream a portion of the water and other monomeric reaction products which have a molecular weight of less than 500;

(E) recycling the second non-permeate stream comprising concentrated chelate aqueous solution to the contacting step (A); and

(F) adding water-soluble alkali to the cyclic process.

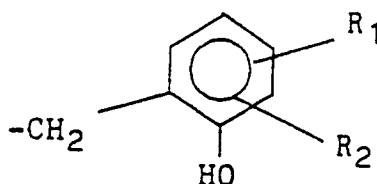
2. The process of Claim 1 wherein the chelate in step (A) is:

(a)



wherein

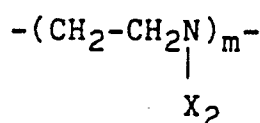
X_1 is independently in each occurrence -H, $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{-P(=O)(OH)}_2$, or



wherein

R_1 and R_2 are independently in each occurrence $-\text{CH}_3$, $-\text{SO}_3\text{H}$, $-\text{Cl}$, $-\text{H}$, $-\text{COOH}$; and m is an integer between 5 and 20,000;

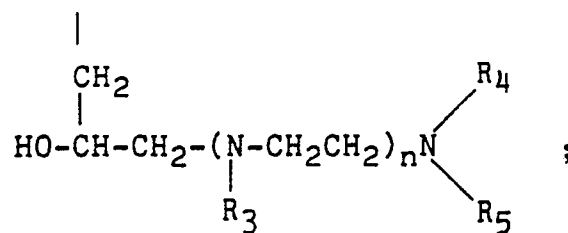
(b)



wherein

X_2 is independently in each occurrence -H, $-\text{CH}_2\text{CH(OH)CH}_2\text{OH}$, $-\text{CH}_2\text{CH(OH)CH}_2\text{Cl}$, or

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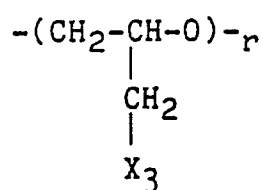


10 R_3 , R_4 and R_5 are independently in each occurrence X_1 , wherein X_1 is as defined hereinabove;
 m is an integer between 5 and 20,000; and
 n is 0, 1, 2, 3 or 4;

(c)

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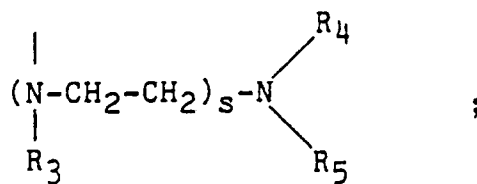
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wherein

25 X_3 is independently in each occurrence -OH, -Cl, or

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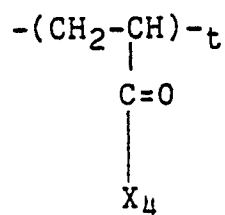


35 R_3 , R_4 and R_5 are as defined hereinabove;
 r is an integer between 10 and 20,000, and
 s is an integer between 1 and 4;

(d)

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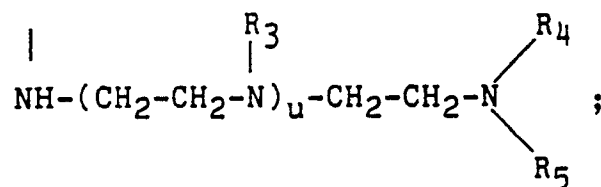
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wherein

50 X_4 is independently in each occurrence -OH, -OCH₃, -OCH₂CH₃, or

55



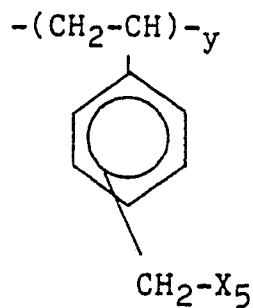
R_3 , R_4 and R_5 are as defined hereinabove;
 t is an integer between 10 and 20,000, and
 u is an integer between 1 and 4;

(e)

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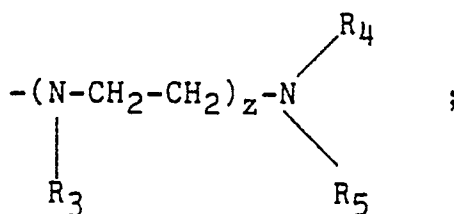


wherein

X_5 is independently in each occurrence -OH, -Cl, or

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R_3 , R_4 and R_5 are as is defined hereinabove;

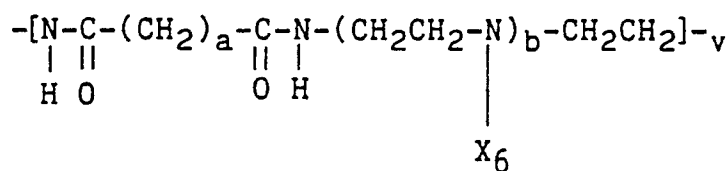
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y is an integer between 10 and 20,000, and

z is an integer between 1 and 4;

(f)

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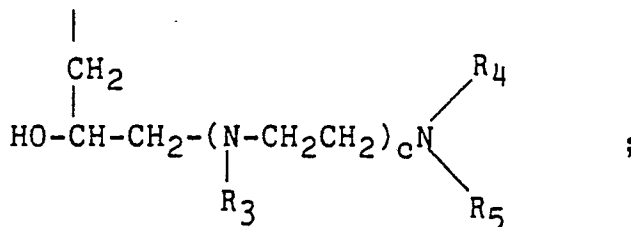
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wherein

X_6 is independently in each occurrence -H, -CH₂CH(OH)CH₂OH, -CH₂CH(OH)CH₂Cl, or

45

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R_3 , R_4 and R_5 are as defined hereinabove;

v is between 10 to 10,000,

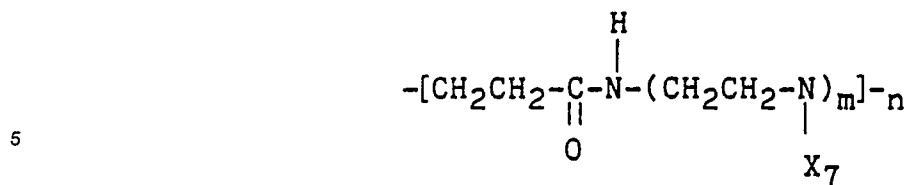
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a is 6,

b is between 1 and 4, and

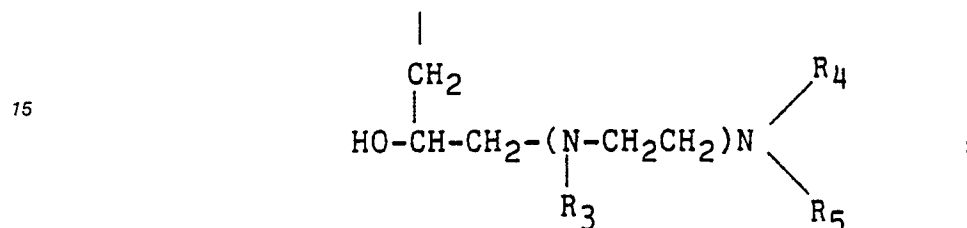
c is between 1 and 4;

(g)

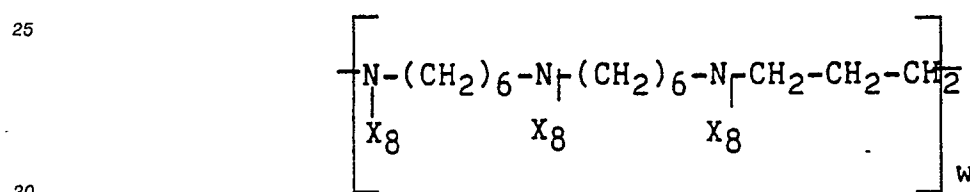


wherein

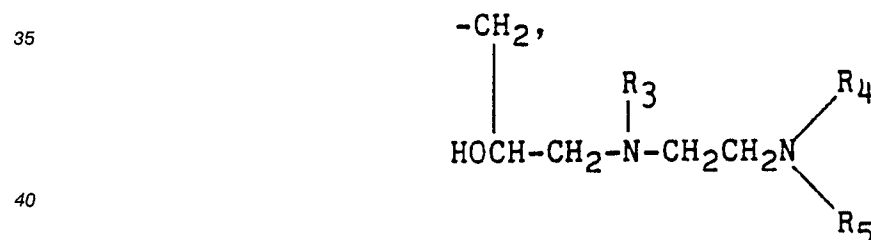
10 X₇ is independently in each occurrence -H, -CH₂CH(OH)CH₂OH, -CH₂CH(OH)CH₂Cl, or



20 m, x, n, R₃, R₄ and R₅ are as defined hereinabove; or
(h)



wherein X₈ is -H, -CH₂CH(OH)CH₂Cl, -CH₂CH(OH), or



wherein

45 R₃, R₄ and R₅ are as defined hereinabove; and
w is between 2000 and 4000.

3. The process of Claim 1 wherein the first and second separation membranes comprise dialysis or ultrafiltration.

4. The process of Claim 3 wherein the first and second membrane separation means comprise ultrafiltration wherein the ultrafiltration membranes possess a molecular weight cutoff of 500 to 30,000 are fabricated from polymers of polysulfones, polyethersulfones, polyamides, cellulosic polymers, polyetherketones, polyolefins, polycarbonates, polyesters, or polyestercarbonates.

5. The process of Claim 1 wherein in step (A) the polyvalent metal ion is selected from the group consisting of iron, copper, cobalt, and manganese.

6. The process of Claim 2 wherein the organic, water-soluble, polymeric chelate possesses a molecular weight of between 1,000 and 500,000.

7. The process of Claim 1 wherein step (A) occurs at temperatures of 10 to 90° C.

8. The process of Claim 7 wherein the concentration of chelating groups in the aqueous reaction

solution of step (A) is 0.01 and to 0.5M.

9. The process of Claim 8 wherein steps (C) and (D) occur at temperatures between 0 and 90 ° C.

10. The process of Claim 9 wherein in step (C) between 15 and 70 volume percent of the aqueous solution is obtained as the first permeate stream.

5 11. The process of Claim 10 wherein in step (C) the amount of calcium oxide added to the first permeate stream is about 1 mole of calcium oxide to one mole of sulfite.

12. The process of Claim 10 wherein in step (D) between 5 and 25 volume percent of the combined first permeate and first non-permeate stream is obtained as the second permeate stream.

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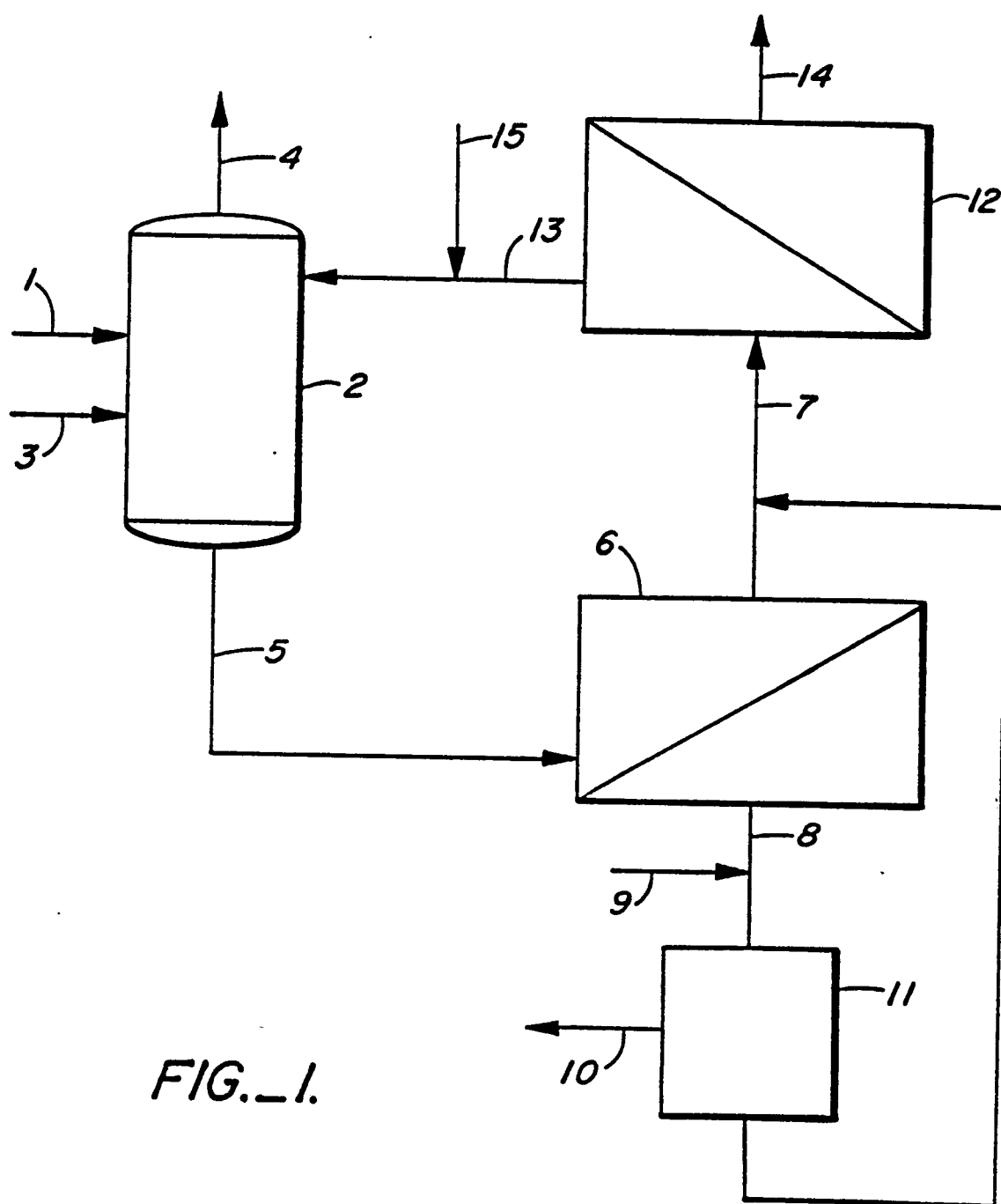


FIG._1.